

MODELING AND ANALYSIS OF DEHYDROGENATION OF CYCLOHEXANE BY EQUILIBRIUM SHIFT IN A PALLADIUM-CERAMIC MEMBRANE REACTOR

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ABSTRACT

Electroless deposition of palladium thin-films on a surface of microporous ceramic substrate has been used to develop a new class of perm-selective inorganic membrane. The membrane, with 9.77 μm palladium film on a ceramic disk was characterized by conducting permeability experiments with pure hydrogen, argon and carbon dioxide and mixtures of hydrogen/nitrogen and hydrogen/methane at temperatures ranging from 473 to 673 K at a trans-membrane pressure differences from 35 to 173 kPa. The results show that the membrane has both high selectivity and permeability for hydrogen and has the potential for application in membrane reactor-separator to enhance productivity in equilibrium limited reactions by equilibrium shift. A model for the single-stage gas permeation for a three component system, without chemical reaction, is developed for cocurrent plug-flow configuration. Analysis shows that the model equations have a singular point. A method is described how to avoid the singular point in order to solve the model equations numerically. A mathematical model is presented, which considers radial diffusion for dehydrogenation of cyclohexane by equilibrium shift in a palladium-ceramic membrane reactor.

INTRODUCTION

The development of high temperature-resistant membranes to recover hydrogen is a topic of considerable scientific interest. Coal gasification and several other high-temperature industrial processes generate hydrogen as a by-product. These processes offer a potentially significant source of hydrogen for use in clean power generation (e.g., fuel cells) and as primary chemical feedstock. In recent years, there has been increased interest in developing inorganic composite membranes for in-situ separation of hydrogen to achieve equilibrium shift in catalytic membrane reactors. The productivity of these membrane reactors, however, has been severely limited by the poor perm-selectivity of the available membranes [1, 2]. To develop a new class of hydrogen perm-selective membrane, we used electroless plating to deposit thin palladium films on a microporous ceramic substrate [3]. In this paper, we present new data for the permeability and selectivity of hydrogen using electroless deposited palladium-ceramic composite membrane for several pairs of gas mixtures.

In one of the earlier studies, Pan & Habgood [4] presented a model to describe permeation through polymeric membrane in a single-stage cocurrent, plug-flow module and showed that the system has a singular point. In their work, they presented results away from the singular point. In this work, we investigated the use of our new palladium-ceramic composite membrane for single-stage gas permeation

for three-component system without reaction. To obtain the numerical results for the whole operating range, special care should be taken to avoid the singular point. This paper presents an analysis to show how to avoid the singular point in numerical computation.

This work also investigates the use of our new palladium-ceramic composite membrane in membrane-reactor configuration for dehydrogenation of cyclohexane by equilibrium shift. The dehydrogenation of hydrocarbons is a class of reactions that have been studied extensively in the past. Several investigators studied the dehydrogenation of cyclohexane in membrane reactor [5-7]. The results show that 100% conversion using vycor-glass membrane, is not possible because the undecomposed feed gas also passes through the porous membrane to the separation side [5, 6]. In one study [7], it was shown that near 100% conversion of cyclohexane to benzene is possible at 473 K and 1 atm by removing hydrogen continuously from the reaction mixture through a thin palladium membrane. Zhao et al. [8] obtained similar results for dehydrogenation of 1-butane to butadiene by using a palladium membrane reactor.

In order to study the actual transport mechanism through the catalyst bed in membrane reactor system, Itoh [9] developed ideal and radial diffusion models to predict the hydrogen flow profile in the catalyst bed of a palladium membrane reactor. Mixture of hydrogen and argon is considered in catalyst side instead of actual reaction. Ideal flow model cannot explain the profile for the unpermeated hydrogen along the reactor length. But radial diffusion model can explain the flow profile. In the present work, a model is developed considering actual reaction, dehydrogenation of cyclohexane, in the catalyst bed and the radial diffusion as well.

MEMBRANE DEVELOPMENT AND CHARACTERIZATION

The details of the preparation and characterization of a thin-film palladium-ceramic composite membrane by electroless deposition process are presented elsewhere [3]. Characterization of the membrane was conducted by testing the permeability for pure hydrogen, helium, argon, carbon dioxide and mixture gases of hydrogen/nitrogen and hydrogen/methane. Permeability experiments were conducted at temperatures ranging from 473 K to 673 K. Feed side pressures ranged from 136 kPa to 274 kPa and permeate side pressure was 101 kPa.

MODEL DEVELOPMENTS

SINGLE-STAGE GAS PERMEATION WITHOUT REACTION

The mathematical formulation for single-stage gas permeation process is based on following assumptions: (a) there are two permeable components a and b , a is more permeable than b , and one non-permeable component i in the system; (b) the permeability of each gas component is the same as that of the pure gas, and is independent of pressure; (c) negligible gas phase concentration gradients exists in the permeation direction; (d) negligible pressure drop in the feed and permeate gas streams; (e) negligible diffusion along the axial flow path; (f) plug flow and ideal gas are assumed for both feed and permeate streams and (g) permeation obeys modified Fick's law. The flow stream and its compositions for co-current flow are shown schematically in Fig. 1.

Using the permeation rate equations and a material balance over the differential area dS , the following differential equations can be obtained:

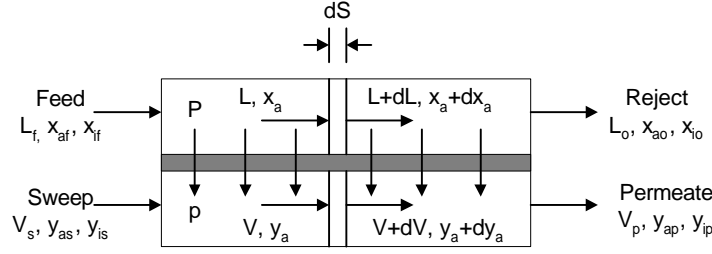


Figure 1: Schematic of cocurrent permeation cell.

$$\begin{aligned} \text{Permeation rate} \quad \int \frac{dV y_a}{dS} &= \int \frac{Q_a}{h} \left[p P x_a g^n - p p y_a g^n \right] \\ \text{eqns. of } a \text{ and } b \quad \int \frac{dV y_b}{dS} &= \int \frac{Q_b}{h} \left[p P x_b g^n - p p y_b g^n \right] \end{aligned} \quad \begin{aligned} \text{Overall material and} \\ \text{component } a \text{ balances} \quad \int dL x_a &= - \int dV y_a \end{aligned} \quad (1)$$

The overall mass and component balances between the inlet and at any arbitrary point along the membrane are given as:

$$\begin{aligned} L_f + V_s &= L + V & L x_i &= L_f x_{if} = \text{constant} \\ L_f x_{af} + V_s y_{as} &= L x_a + V y_a & V y_i &= V_s y_{is} = \text{constant} \end{aligned} \quad (2)$$

Combining Eqns. (1) and (2), and defining selectivity, $a = Q_a / Q_b$, pressure ratio, $g = p / P$, flow rate ratio, $F_f = V_s / L_f$, and dimensionless membrane area, $R = Q_a P^n S / h L_f$, one can obtain the following differential equations::

$$\frac{dy_a}{dx_a} = \frac{y_a - x_{af} + F_f [y_a - y_{as}] \left[a e^{x_a^n} - b g y_a g^n \right] [1 - y_a] - e^{x_b^n} - b g y_b g^n y_a}{x_a - x_{af} + F_f [x_a - y_{as}] \left[a e^{x_a^n} - b g y_a g^n \right] [1 - x_a] - e^{x_b^n} - b g y_b g^n x_a} \quad (3)$$

$$\frac{dR}{dx_a} = \frac{a [y_a - x_{af} + F_f [y_a - y_{as}]]}{[x_a - y_a] \left[a e^{x_a^n} - b g y_a g^n \right] [1 - x_a] - e^{x_b^n} - b g y_b g^n x_a} \quad (4)$$

Eqns. (3) and (4) were solved by the Runge-Kutta-Gill method as an initial value problem with the boundary conditions:

$$\text{At } R = 0: \quad \begin{cases} L = L_f; & x_a = x_{af}; & x_i = x_{if} \\ V = V_s; & y_a = y_{as}; & y_i = y_{is} \end{cases} \quad (5)$$

For the special case of no sweep gas on the permeate side, y_{as} can not be specified and must be determined by Eqns. (3) and (4) subject to boundary conditions, Eqn.(5), where $V_s = 0$ and $y_{is} = 0$. At the feed inlet, y_{as} can be expressed as:

$$\frac{y_{as}}{1 - y_{as}} = a \frac{x_{af}^n - b g y_{as} g^n}{x_{bf}^n - b g y_{bs} g^n} \quad (6)$$

It is noted that Eqn.(3) appears to be indeterminate at the feed inlet for no sweep gas. Using L'Hospital's rule, the differential equation at the feed inlet can be obtained as:

$$\left. \frac{dy_a}{dx_a} \right|_f = \frac{(y_{as} - x_{af}) \left[n a y_{bs} x_{af}^{n-1} + n y_{as} x_{bf}^{n-1} \right] - n y_{as} x_{if} x_{bf}^{n-1}}{a A_f (1 - x_{af}) - x_{af} B_f + (y_{as} - x_{af}) \left[a A_f + B_f + n g^n (y_{as} y_{bs}^{n-1} + a y_{bs} y_{as}^{n-1}) \right]} \quad (7)$$

where $A_f = x_{af}^n - g y_{as} g^n$ and $B_f = x_{bf}^n - g y_{bs} g^n$.

DEHYDROGENATION OF CYCLOHEXANE USING Pd-CERAMIC COMPOSITE MEMBRANE REACTOR

The newly developed palladium-ceramic composite membrane is currently being theoretically studied in membrane reactor configuration for dehydrogenation of cyclohexane. In the model, Pt-Al₂O₃ catalyst pellets are assumed to be inside the palladium-ceramic membrane tube. Argon is used as carrier gas in the reaction side and as the sweep gas in separation side. The hydrogen produced by the reaction permeates through the membrane into the shell side and the rate equation is given by [7]:

$$r_c = \frac{-k \left(K_P P_C / P_H^3 - P_B \right)}{1 + K_B K_P P_C / P_H^3} \quad (8)$$

The concentration of hydrogen near the membrane wall is depleted by permeation. As a result, a concentration gradient occurs in the radial direction. To model radial diffusion, two-dimensional pseudo-homogeneous model is used to describe the transport mechanism through the catalyst bed. A schematic of the catalytic packed-bed membrane reactor is shown in Fig. 2

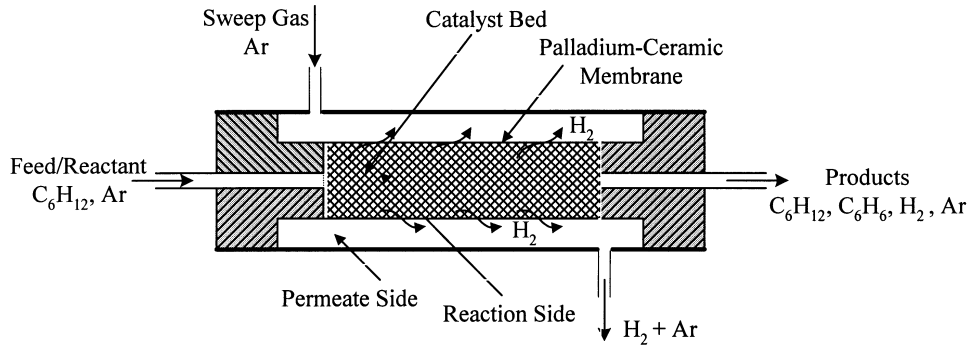


Figure 2: Schematic of a membrane reactor-separator using Pd-ceramic composite membrane.

The model for membrane reactor is based on the following assumptions: (a) isothermal, isobaric and steady-state flow through the reactor (both the packed bed and separation sides), (b) ideal gas behavior, (c) flat concentration profile in separation side, (d) concentration profiles in reaction side are not flat due to permeation of hydrogen, (e) negligible axial diffusion, and (g) the amount of dehydrogenation taking place on the palladium-ceramic tube is negligibly small compared to that on the catalyst pellet surface. The basic partial differential equations for different components in reaction side may be derived in dimensionless form as:

$$\frac{\partial U \Phi_i}{\partial Z} = \frac{d_p l_0}{Pe_r g_i r_1^2} \left[\frac{1}{R} \frac{\partial \Phi_i}{\partial R} + \frac{\partial^2 \Phi_i}{\partial R^2} \right] + a_j \quad (9)$$

where j is the reaction term and i is the component name as defined in the nomenclature section. The stoichiometric coefficient, a_i is positive for a product, negative for a reactant and zero for any inert. The equation set, Eqn. (9) can be solved subject to following boundary and initial conditions:

$$\begin{aligned} \text{At } R = 0, 0 \leq Z \leq 1: \quad & \frac{\partial \Phi_i}{\partial R} = 0; \quad \text{for all components} \\ \text{At } R = 1, 0 \leq Z \leq 1: \quad & \left\{ \begin{array}{l} \frac{\partial \Phi_A}{\partial R} = 0; \quad \frac{\partial \Phi_B}{\partial R} = 0 \\ \frac{\partial \Phi_C}{\partial R} = 0; \quad \frac{\partial \Phi_H}{\partial R} = b(\Phi_H^n - f_H^n) \end{array} \right. \end{aligned} \quad (10)$$

$$\text{At } Z = 0, \text{ Reaction side: } 0 \leq R \leq 1: \left\{ \begin{array}{l} \Phi_A = \Phi_A^o; \quad \Phi_B = 0 \\ \Phi_C = \Phi_C^o; \quad \Phi_H = 0 \end{array} \right. \quad \text{Separation side: } f_A = f_A^o; f_H = 0 \quad (11)$$

Equation set, Eqn. (9) were solved numerically using a finite difference method subject to the conditions in Eqns. (10) and (11).

RESULTS AND DISCUSSION

PERMEABILITY OF PURE GASES

Table 1 shows the values of Q_H and n obtained for hydrogen using the membrane, with 9.77 mm palladium film, developed in this study. The Q_H and n are determined from nonlinear regression of Eqn. (12) with known flux and partial pressures of hydrogen on both sides of membrane. The n decreases and Q_H increases with increasing temperature.

$$N_H = \frac{Q_H}{h} (P_H^n - p_H^n) \quad (12)$$

In Fig. 3, the results of permeability experiment for hydrogen with the 9.77 mm palladium film membrane are shown for three different temperatures. The n value used in the figure is the value which best fits the combined temperature data. The best fit n values for hydrogen, helium, argon and carbon dioxide are 0.513, 1.1, 1.81 and 1.81 respectively. Figure 3 shows that flux increases with increasing temperature at a given driving force $(P_H^{0.513} - p_H^{0.513})$. Therefore, the composite membrane favors high temperature gas separation.

Table 1. Hydrogen permeabilities and power-index at different temperatures for Pd-ceramic composite membrane with 9.77 mm palladium film.

Temperature (K)	Permeability Q_H (moles / m · s · Pa ⁿ)	Power Index n
473	1.653×10^{-8}	0.537
573	2.637×10^{-8}	0.513
673	4.158×10^{-8}	0.501

PERMEABILITY OF MIXTURE GASES

Experiments with feed gas mixtures of H_2/N_2 and H_2/CH_4 were conducted to test the presence of gas-phase mass transfer resistance. The experimental conditions were same as for pure gases. Figure 4 shows the results of hydrogen permeability experiments for a H_2/N_2 mixture. The results show that n values of hydrogen in mixture gases are higher than n value of pure hydrogen. For H_2/N_2 and H_2/CH_4 mixtures, n values are 0.623 and 0.564 respectively. Accumulation of non-diffusing gas on feed side of the membrane restricts hydrogen diffusion and thus gives the higher values of n .

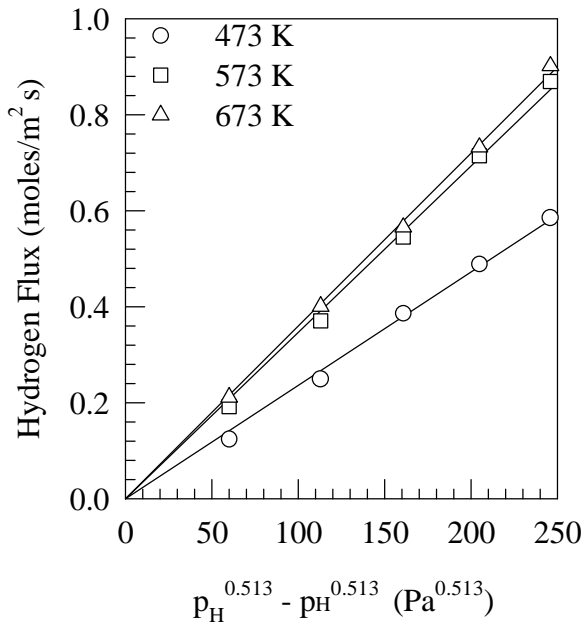


Figure 3: Effect of driving force on hydrogen flux at various temperatures through Pd-ceramic membrane with 9.77 μm palladium film for pure hydrogen gas.

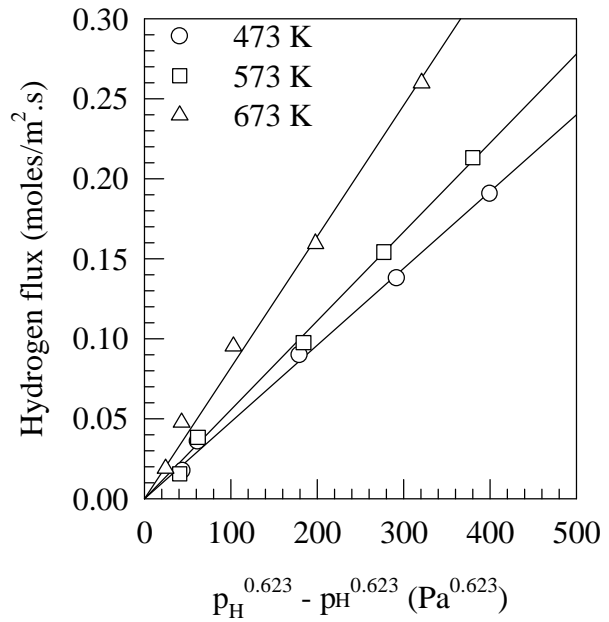


Figure 4: Effect of driving force on hydrogen flux at various temperatures through Pd-ceramic membrane with 9.77 μm palladium film for hydrogen/nitrogen gas mixture.

SELECTIVITY OF HYDROGEN

The selectivity of hydrogen is defined as the ratio of the hydrogen flux to the flux of another less permeable gas at the same trans-membrane pressure difference [2]. Based on this definition, the selectivities of H_2/Ar and H_2/CO_2 for the composite membrane were determined. Figure 5 shows the selectivity results for H_2/CO_2 . For the pressure difference of 35 to 173 kPa, the selectivities of H_2/Ar and H_2/CO_2 change from infinity to 600 at 473 K. It indicates the leakage through membrane defects is minimal. Figure 5 shows that the selectivity for H_2/CO_2 decreases with increasing pressure difference. This was expected because permeation rate for CO_2 , through the membrane was proportional to a high power $[n = 1.81]$ of pressure.

EXPERIMENTAL RESULTS AND MODEL PREDICTIONS

The membrane separation model was used to predict the hydrogen mole fraction in the permeate and reject streams. Figure 6 compares experiment data for H_2 / N_2 mixture at 573 K, to model prediction at the same stage cut. Predicted product purity was higher than the actual product purity and hydrogen mole fraction was lower than actual mole fraction in reject stream. The result confirms that the non-diffusing gas on both sides of membrane restricts hydrogen diffusion. Since the difference between predicted and actual mole fraction is less than 12%, the model is relatively accurate in predicting the data obtained from permeability experiments.

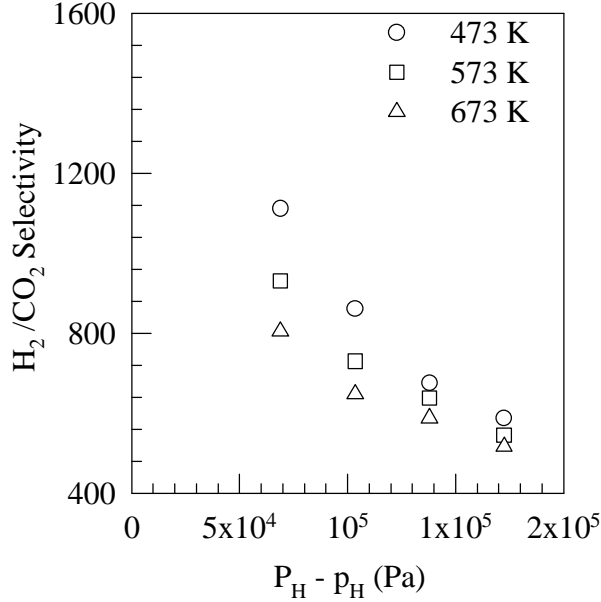


Figure 5: Effect of trans-membrane pressure difference on H_2 / CO_2 selectivity at various temperatures for Pd-ceramic membrane with 9.77 μm palladium film.

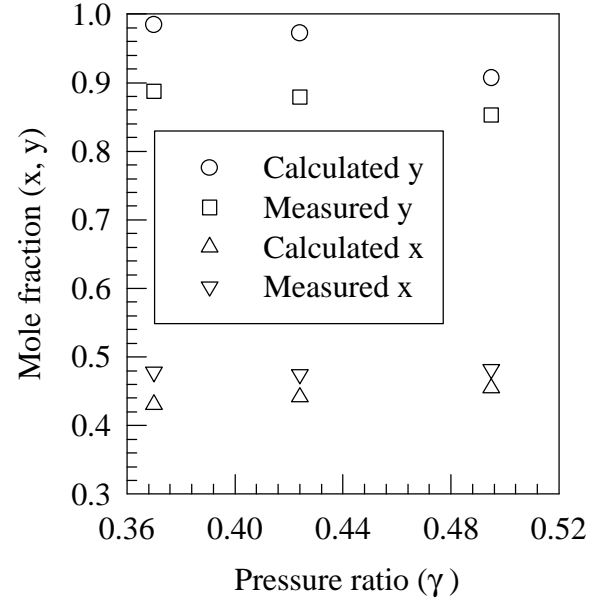


Figure 6: Effect of pressure ratios on permeate and reject compositions at 573 K compared to model calculations for Pd-ceramic membrane with 9.77 μm Pd-film for H_2 / N_2 gas mixture.

MODEL ANALYSIS FROM THE VIEWPOINT OF STABILITY

Equations (3) and (4) appear to be indeterminate at the singular point: $x_a = y_a = (x_{af} + y_{as}F_f) / (1 + F_f)$.

Numerical scheme becomes unstable at this point. Pan and Habgood [4] also identified the same singular point. Their analysis, however was away from singular point. One can avoid this singular point by an appropriate selection of the operating variables. Following example will illustrate this phenomenon.

Example:

Feed Gas Condition	Sweep Gas Condition	Parameters
$x_{af} = 0.71$	$y_{as} = 0.26$	$n = 1.0$
$x_{if} = 0.08$	$y_{is} = 0.30$	$a = 650$
$L_f = 1.0$	$V_s = 2.0$	$g = 0.1$

At this condition, singular point is:

$$x_a = y_a = 0.41$$

Figure 7 shows plots of reject x_a and permeate y_a mole fractions as a function of dimensionless membrane area, R . The plots intersect at the singular point, where $x_a = y_a = 0.41$. This singular point can be avoided if composition of the more permeable component in feed gas and sweep gas is at either side of this point. So, there are two regions for which singular point will not arise: i) if $y_{as} > x_{af}$, then the composition of the more permeable component in sweep gas is greater than that in the feed inlet; and ii) if $y_{ap} < x_{ao}$, then the composition of more permeable component in permeate is less than that in the retentate.

The following procedure can be used to obtain numerical results for the whole range of stage cuts. Generally, an increment, like 10^{-n} with an integer exponent is used. As the singular point is approached, the numerical method will fail. In that case if one uses a factor 1.1, 1.3, 1.7 etc. with 10^{-n} , the instability can be avoided. The data reveals that there are some discrepancies around the singular point (Figure 8).

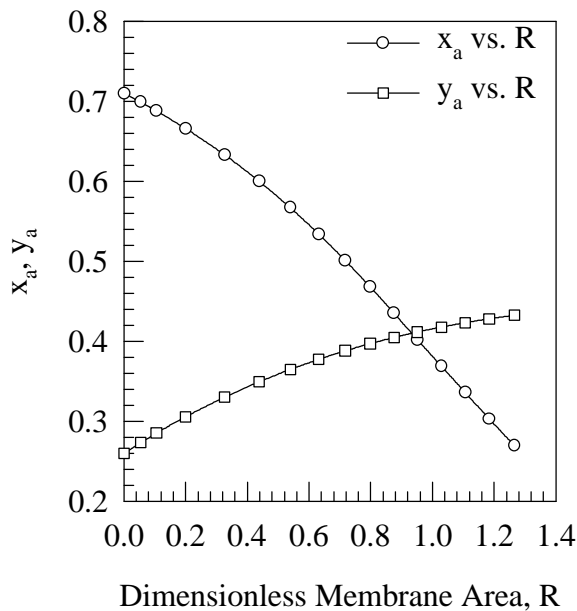


Figure 7: Reject and permeate mole fractions as function of dimensionless membrane area.

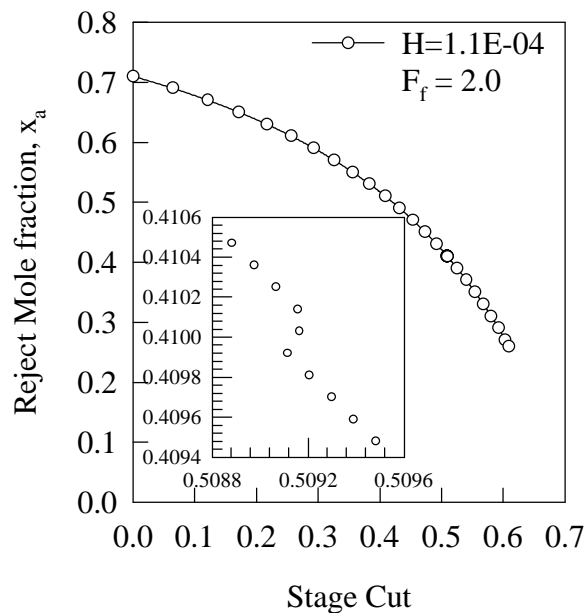


Figure 8: Effect of stage cut on reject mole fraction for cocurrent flow (singularity is shown in the insert figure).

CONCLUSIONS

The thin-film, palladium-ceramic composite membrane fabricated in this work has a high permeability and selectivity for hydrogen at elevated temperature. These properties makes it an ideal candidate for use in membrane reactors for equilibrium limited dehydrogenation reactions. Experimental results show that n values of hydrogen in mixture gases are higher than n values of pure hydrogen. This means that accumulation of non-diffusing gas on feed side of the membrane restricts hydrogen diffusion. For the same reason, a mathematical model for single-stage gas permeation predicts higher product purity than actual purity. To model radial diffusion, a two-dimensional pseudo-homogeneous model is developed for dehydrogenation of cyclohexane in a membrane reactor using the newly developed membrane. The newly developed radial-diffusion model accurately describes membrane reactor performance.

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NOMENCLATURE

$D_{er,i}$	Effective radial diffusion coefficient of i component in the packed bed, [m^2 / s]
d_p	Sphere-equivalent diameter of cylindrical catalyst, [m]
F_f	Flow rate ratio, V_s / L_f
h	Membrane thickness, [m]
K_B	Adsorption equilibrium constant of benzene, [Pa^{-1}]
K_p	Pressure equilibrium constant, [Pa^3]
k	Rate constant, [$\text{mol} / \text{m}^2 \cdot \text{s} \cdot \text{Pa}$]
L	Feed side flow rate, [mol / s]
L_f	Feed flow rate, [mol / s]
$[l_0]$	Entire length of palladium membrane, [m]
N_H	Permeation flux of hydrogen, [$\text{mol} / \text{m}^2 \cdot \text{s}$]
n	Power index for permeation rate, dimensionless
P	Feed or reaction side total pressure, [Pa]
P_i	Partial pressure of i component on reaction side, [Pa]
$Pe_{r,i}$	Peclet number for i component in packed bed, $u_0 d_p / D_{er,i}$
P_0	Reference pressure, 1.013×10^5 Pa
p	Separation side total pressure, [Pa]
p_i	Partial pressure of i component on separation side, [Pa]
Q_s	Permeability of component (a = more permeable, b = less permeable), [$\text{mol} / \text{m} \cdot \text{s} \cdot \text{Pa}^n$]
R	Dimensionless membrane area, dimensionless radial distance, [r / r_1]
R_g	Gas constant, [$\text{kJ} / \text{mol} \cdot \text{K}$] or [$\text{m}^3 \cdot \text{Pa} / \text{mol} \cdot \text{K}$]
r	Radial distance from the center of packed bed, [m]
r_1	Inner radius of membrane tube, [m]
r_2	Outer radius of membrane tube, [m]
r_3	Inner radius of shell tube, [m]
r_C	Reaction rate of cyclohexane, [$\text{mol} / \text{m}^3 \cdot \text{s}$]
S	Membrane area, [m^2]
u	Interstitial velocity of gas on reaction side, [m / s]
u_0	u at inlet of reaction side, [m / s]
U	Dimensionless total gas flow rate on reaction side, [u / u_0]
V	Permeate side flow rate, [mol / s]

V_s	Sweep gas flow rate, [mol / s]
x_s	Mole fraction of component in feed side stream (a = more permeable, i = non-permeable)
x_{as}	Mole fraction of more permeable component a (f = feed stream, 0 = reject stream)
x_{sf}	Mole fraction of component in feed stream (a = more permeable, i = non-permeable)
y_s	Mole fraction of component in permeation side stream (a = more permeable, i = non-permeable)
y_{as}	Mole fraction of more permeable component a (s = sweep stream, p = permeate stream)
Z	Dimensionless reactor length, [z / l_0]
z	Length of palladium membrane, [m]
\mathbf{a}	Ratio of permeability, [Q_a / Q_b]
\mathbf{a}_i	Stoichiometric coefficients
b	Defined as $\frac{r_1}{r_2 - r_1} \frac{R_g T Q_H}{P_0^{1-n} D_{er} \int_H}$
g	Ratio of permeate to feed pressure
Φ_i	Dimensionless partial pressure of i component on reaction side, P_i / P_0
Φ_i^0	Dimensionless partial pressure of i component on reaction-side inlet
f_i	Dimensionless partial pressure of i component on separation side, p_i / P_0
f_i^0	Dimensionless partial pressure of i component on separation-side inlet
j	Dimensionless source term, $\frac{R_g T l_0}{u_0 P_0} \frac{k [K_P \mathbf{a}_C - P_0^3 \mathbf{a}_H^3 \mathbf{a}_B]}{P_0^3 \mathbf{a}_H^3 + K_B K_P \mathbf{a}_C}$

Subscripts

i A = argon, B = benzene, C = cyclohexane, and H = hydrogen

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